The high-pressure behaviour of 3R-NbS$_2$

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Abstract. The high pressure behaviour of 3R-NbS$_2$ has been investigated by angle-dispersive X-ray powder diffraction using diamond anvil cells up to 14 GPa. The compression behaviour of the structure is highly anisotropic. The compressibility perpendicular to the layers is 2.5 times higher than within the layers. A fit of a 3rd-order Birch-Murnaghan equation of state gave a volume at zero pressure V_0=174(1) Å^3 and a bulk modulus b_0=57(1) GPa, with a pressure derivative b'=8.6(5).

Introduction

Transition metal dichalcogenides and their intercalation compounds attracted significant attention due to their superconductivity [1] and their potential use in solid state batteries [2] and catalytic processes in petrochemical industry [3]. NbS$_2$ crystallises in a quasi two dimensional structure. Layers of trigonal edge-sharing NbS$_6$ prisms are stacked onto each other along the [001] direction. The intra-layer bonding is predominantly covalent, whereas the layers are connected by van-der-Waals forces. Different stacking sequences of the NbS$_2$ layers lead to the formation of two polytypes, the hexagonal 2H-NbS$_2$ [4] with two NbS$_2$ layers, and the rhombohedral 3R-NbS$_2$ [5, 6] with three layers per unit cell, according to the modified Gard notation [7]. The 3R polymorph crystallises in the space group $R3m$ (no. 160) with the unit cell parameters of a=3.3285(4) and c=17.910(4) Å. All atoms are located on the Wyckoff position 3a (0,0,z) with z=0 for niobium and z=0.2464(1) and 0.4201(2) for the sulphur atoms, respectively [5, 6]. The layer structure causes a strong anisotropy in the physical properties e.g. resistivity and compressibility [1, 9]. At ambient conditions NbS$_2$ is a metal [8].

The effect of pressure on the critical temperature of superconductivity, as well as the compressibility of 3R-NbS$_2$ has been investigated up to 1 GPa [9]. The authors found the linear compressibilities k∥a=0.0016(4) GPa^{-1} and k∥c=0.011(4) GPa^{-1} from their X-ray diffraction measurement using a piston-cylinder apparatus and a slight pressure dependence of the superconducting transition temperature T$_c$. However, the extension of the pressure range beyond 1 GPa is of interest, because pressure leads to changes in the electronic bands, which may be associated with a structural phase transition [10].

Here we present the results of a high-pressure X-ray powder diffraction study on 3R-NbS$_2$ up to 14 GPa.

Experimental

The sample of 3R-NbS$_2$ was prepared by sintering a stoichiometric mixture of the elements for 10 days at 1125 K. The composition of the sample was verified by electron microprobe analysis using a Cameca "Camebax Microbeam". The polytype of the sample was determined by conventional powder diffraction. The high pressure data were collected with a MAR 2000 image plate diffractometer with a wavelength of 0.5608 Å (Ag K$_\alpha$). A silicon (111) monochromator was applied in the incident beam for the suppression of the background and $\lambda/2$ reflections from the gasket material. Pressure was applied through a Merrill-Bassett type diamond anvil cell [11] with an Inconel gasket. As the pressure transmitting medium a 16:3:1 mixture of methanol:ethanol:water was used [12]. The ruby fluorescence method using the pressure scale of Piermarini *et al.* [13] was used to determine the pressure. The sample to detector distance was determined by measuring the sample in the uncompressed cell. The geometry correction for the radial integration of the two-dimensional data and the transformation into standard one-dimensional powder patterns were performed using FIT2D [14]. The single reflections were fitted with Gaussian peak shape function and a 3rd-order polynom for the background with the program MFIT [15]. The unit cell parameters were calculated using the refinement program REFCEL [16].

Results and Discussion

Diffraction patterns were collected up to 14 GPa. The pressure dependence of the normalised lattice parameters a/a$_0$ and c/c$_0$ and of the unit cell volume are given in figures 1 and 2, respectively.

A 3rd-order Birch-Murnaghan equation-of-state was used to determine the unit cell volume at pressure of 0 GPa, V_0, the bulk modulus b_0 and its pressure dependence $b' = \partial b_0/\partial p$ [17]. Values of V_0=174(1) Å^3, b_0=57(1) GPa and b'=8.6(5) were obtained. V_0 agrees well with the data given by Morosin

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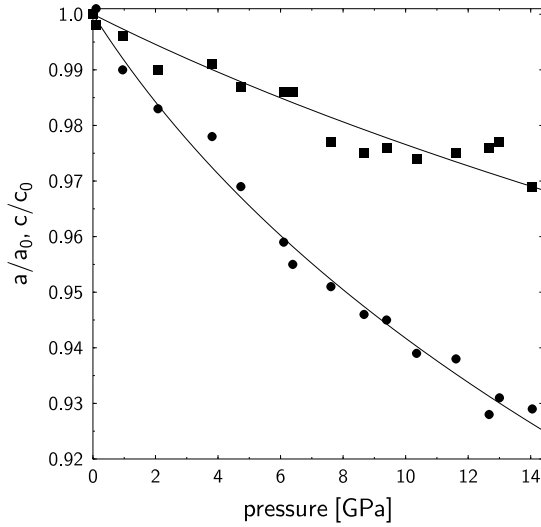
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Fig. 1. Variation of the normalised cell parameters for 3R-NbS$_2$ with pressure. The squares correspond to a/a$_0$ and the circles represent c/c$_0$. The experimental errors bars correspond to the size of the symbols. The lines are guides for the eyes.
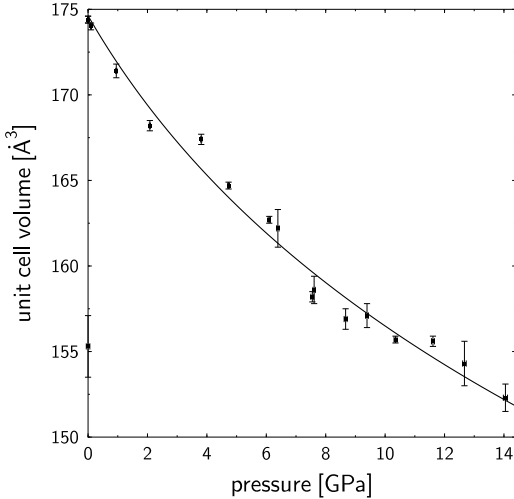

Fig. 2. Pressure dependence of the unit cell volume of 3R-NbS$_2$. The line is a fit of a 3rd-order Birch-Murnaghan equation-of-state to the data points.

[5] and Powell and Jacobson [6] for the unit cell volume at ambient conditions. The linear compressibility k was derived by fitting linear functions to the unit-cell parameters a and c at pressures up to 1.5 GPa. The resulting values are given in table 1. The compression behaviour is highly anisotropic with compressibility parallel to the c axis being 2.5 times higher than parallel the a axis. The anisotropy of the compression is in the order of magnitude for related transition-metal dichalcogenides e.g. TiS$_2$ [18], 2H-MoS$_2$ [20, 21] and

2H-NbSe$_2$ [9, 21] but less pronounced than in SnS$_2$ [19] (see table 1).

The data for the linear compressibilities for 3R-NbS$_2$ given by Jones et al. [9] are in good agreement with our values for the c direction. However, the k‖a values differ by a factor of two. The compressibility data for 2H-NbSe$_2$ given by Flack [21] and Jones et al. [9] are likewise significantly different. Hence, one might attribute the differences in the linear compressibilities along the a axis to experimental uncertainties in the work of Jones et al. [9].

Table 1. Values for the linear compressibility parallel to the a and c axis for several metal dichalcogenides.

	k‖a [GPa^{-1}]	k‖c [GPa^{-1}]	Reference
3R-NbS$_2$	0.0039(3)	0.010(4)	this work
3R-NbS$_2$	0.0016(4)	0.011(4)	[9]
1T-TiS$_2$	0.0043(3)	0.017(2)	[18]
1T-SnS$_2$	0.0022(4)	0.025(5)	[19]
2H-MoS$_2$	0.0034(1)	0.0164(3)	[20]
2H-MoS$_2$	0.0033(1)	0.0170(2)	[21]
2H-NbSe$_2$	0.0041(4)	0.0162(5)	[9]
2H-NbSe$_2$	0.0015(3)	0.011(1)	[21]

The strong anisotropy in the compression can be understood by considering of the different types of bonding in the structure. The lowest compressibility is found parallel to the a axis, where the structure consists of layers of covalent bonded trigonal NbS$_6$ prisms, whereas the layers are connected by van-der-Waals forces along the c direction. The compressibility parallel to the stacking direction c is 2.5 times stronger. This can be attributed to the ease with which the distance between the van-der-Waals bonded layers can be reduced compared to distorting the covalent bonded trigonal prisms which would require considerably more energy. In the pressure range investigated, the data reveal that there is no phase transition or discontinuity in the compression of 3R-NbS$_2$.

Unfortunately, the quality of the data was not sufficient for a structure refinement. However, considering closely related structures e.g. TiS$_2$ [18] and SnS$_2$ [19] the following compression mechanism is proposed: The reduction of the van-der-Waals gap is the main compression mechanism, manifested in the strong change of the interlayer S-S distances. The lengths of covalent metal-sulphur bonds in the layers should remain almost constant. Therefore, the compression in the a direction should result in slight changes in the metal-sulphur angles in the trigonal prisms, resulting in an expansion of the layer-thickness under pressure. This mechanism is additionally supported by force field calculations on 2H-MoS$_2$ [20].

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